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Embedded Hydrogen Chloride and Smoke Particle Characteristics During Combustion of Polyvinyl Chloride and Chlorinated Mine Materials

By Maria I. De Rosa and Charles D. Litton

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg/g	milligram per gram
cm	centimeter	μg/g	microgram per gram
cm^2/p	square centimeter per particle	min	minute
$cm^2/(p \cdot g)$	square centimeter per particle per gram	μm	micrometer
ft	foot	p/cm^2	particle per square centimeter
g	gram	p/cm^3	particle per cubic centimeter
in	inch	pct	percent
L	liter	ppm	part per million
L/min	liter per minute	ppm/g	part per million per gram

EMBEDDED HYDROGEN CHLORIDE AND SMOKE PARTICLE CHARACTERISTICS DURING COMBUSTION OF POLYVINYL CHLORIDE AND CHLORINATED MINE MATERIALS

By Maria I. De Rosa[1] and Charles D. Litton[2]

ABSTRACT

The U.S. Bureau of Mines performed experiments to determine the embedded hydrogen chloride (HCl) and smoke particle characteristics during combustion of polyvinyl chloride (PVC) and chlorinated mine materials for development of a test parameter.

The experiments were conducted in an approximately 20-L furnace at set furnace temperatures of 250° and 1,000° C, for a 14-min duration, with an airflow through the furnace of 10 L/min. The variables studied, as a function of time, were hydrogen chloride embedded on smoke particles, hydrogen chloride concentrations in the gas phase, smoke particle average diameter (d_g) and particle concentration (n_o), and product of smoke particle diameter and concentration ($d_g n_o$). Other variables included carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2) concentrations; sample mass weight loss; and furnace temperatures.

Results show that there is a correlation between embedded hydrogen chloride, hydrogen chloride gas concentrations, and inverse of the smoke particle diameter-concentration product ($1/d_g n_o$); the higher the hydrogen chloride gas concentrations, the higher the embedded hydrogen chloride, the higher the $1/(d_g n_o)$ values. These correlations will enable development of a simple test parameter to assess the toxic hazard that these materials pose during fire.

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INTRODUCTION

In 1984, the U.S. Bureau of Mines, within its mission to create and maintain safety in the mines and, specifically, to assess the hazard of mine materials during fire, initiated a series of experiments to characterize smoke particles and primary gas toxicities evolved during the combustion of mine materials. It was found that smoke particles produced by different combustibles differed in average diameter (d_g) and concentration (n_o), and product of diameter and concentration ($d_g n_o$) (*1-2*).[3] Furthermore, it was found that the smoke particle characteristic, $d_g n_o$, varied with the hydrogen chloride gas concentrations produced during the combustion of PVC and chlorinated materials; the higher the hydrogen chloride concentrations, the lower the $d_g n_o$ values (*3*). It may be reasoned that at a low value of $d_g n_o$ (or at a higher value of its inverse, $1/d_g n_o$) a larger percentage of the consumed mass is available for hydrogen chloride production, depending on the chlorine (Cl_2) content of the material, rather than for smoke production.

In subsequent studies (*4-7*), correlations were established between the inverse of the smoke particle diameter-concentration product, $1/d_g n_o$, and the primary gas (hydrogen chloride) evolved during the early combustion of PVC, neoprene, and styrene-butadiene rubber (SBR) mine conveyor belts; PVC and chlorinated mine brattices; and chlorinated polyester-reinforced mine ventilation ducts.

In the present study, the Bureau set out to determine and correlate the embedded hydrogen chloride on smoke particles, the hydrogen chloride concentrations in the gas phase, and the smoke particle characteristics during the combustion of PVC and chlorinated mine materials. These correlations may lead to the development of a test parameter to assess simply and inexpensively the toxic hazard of these materials during fire.

BACKGROUND

The role of aerosols in the transport of irritant gases and their concentrations into the lungs are of interest in inhalation of smoke generated in fires because the irritant gases, loosely bound to the aerosol, are easily removed once they have reached the lower respiratory tract. Other important variables include irritant gas concentrations, aerosol particle sizes, and gas composition. In considering fire situations in mining spaces where polyvinyl chloride and chlorinated materials abound, smoke aerosol could be particularly effective in transporting hydrogen chloride to the respiratory defenses, creating a potential synergistic effect of the aerosol in the presence of toxic gas molecules (*8*). In fact, it has been observed that the toxicity of irritant gases is altered by the presence of aerosols. This alteration, either a decrease or increase in effect, was related to penetration of the respiratory system by the aerosol particles and the gas molecules involved; physical combination between gas and aerosol must occur in order to cause a change in toxicity (*9*). Thus, the penetration of a water-soluble gas such as hydrogen chloride normally trapped in the upper respiratory system, would be enhanced if the gas were absorbed on a properly sized aerosol. It has been reported that 20 to 40 pct of soot particles, with a size ranging from 0.1 to 2.5 μm diam, would be expected to enter the lower lungs and be retained in the alveolar sacs (*10*).

During combustion, the chloride from PVC and chlorinated combustible materials can be found mostly as a volatile chloride compound in the gas phase and, in smaller quantity, as a volatile chloride compound easily absorbed from and/or tightly bound to the soot comprised of roughly spherical particles ranging from 0.03 to 0.11 μm diam (*11*).

In the present study, samples of PVC, neoprene, and SBR mine conveyor belts; PVC and chlorinated fiberglass mine brattices; and chlorinated polyester-reinforced mine ventilation ducts were used during the experiments.

Conveyor belts are complex mixtures of a variety of components. The belt most widely used in mines contain either a halogenated-base polymer (PVC and neoprene) or a halogenated additive (SBR) added to impart fire resistance. Because of economic considerations, PVC resin probably is the most widely used of the halogenated polymers. However, this polymer releases hydrogen chloride at temperatures as low as 180° C, and the reaction is accelerated in oxidizing atmospheres; oxygen plays a catalytic role during the degradation by assisting the dehydrochlorination and product elimination and by increasing the number of initiation sites (*12*). For pure resin, hydrogen

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

chloride is the only product (90 pct) evolved at temperatures below 200° C (*13*); its release depends on the chlorine content of the material, material burning rates, the amount of material present, and the vicinity of the material to the fire source (*4-7*).

At 300° C, the main toxic risk from PVC decomposition products is hydrogen chloride. Hydrogen chloride, with a short-term exposure limit (STEL) of 25 ppm and immediately dangerous to life and health (IDLH) at 100 ppm, is both a sensory and pulmonary irritant. As a sensory irritant of the upper respiratory tract, hydrogen chloride depresses the respiratory rate; the sensory effect is rapid and concentration dependent. As a pulmonary irritant, hydrogen chloride causes severe damage to the lower respiratory tract. Alarie (*14*) found that HCl LC50 (lethal concentration at which 50 pct of laboratory animals die) for noncannulated laboratory animals was of 10,000 ppm as compared with HCl LC50 of only 1,100 ppm for cannulated laboratory animals; (laboratory animals tend to breathe through the nose and humans tend to breathe through the mouth in the presence of this gas). Furthermore, PVC can produce large amounts of particulate matter, the actual amount depending on the conditions (oxygen) of combustion, on whose surface hydrogen chloride is absorbed and transported (*15*). The pulmonary damage from PVC smoke inhalation has been shown to be more severe than from hydrogen chloride alone, probably because the particulates may be drawn into and deposited in the lungs where the absorbed and/or dissolved hydrogen chloride enhances the toxic effects. The HCl LC50 has been found to decrease from 5,600 ppm for pure hydrogen chloride gas to 1,900 ppm for PVC combustion products (*16*).

Neoprene, because of its chlorine content, exhibits flame-retardant characteristics. Although considered thermally stable up to 300° C, neoprene has been found to degrade at 180° C (*17*). The onset temperature for cured compositions could be as low as 125° C. For neoprene, as for PVC, hydrogen chloride is the major degradation toxic product during the early stage of combustion; at 250° C, it accounts for 80 pct of the chlorine present, with the remainder liberated in the form of chlorinated materials. At higher temperatures, carbon monoxide is liberated in large quantities because of gross degradation of the material (*4-7*).

SBR raw gum is flammable and requires large quantities of chlorinated additives, in addition to fillers, plasticizers, and sulfur organic activators; its final degradation products derive from all these constituents. The major toxic component, during the early stage of combustion, is again hydrogen chloride, although in much smaller quantities than PVC and neoprene.

PVC mine brattices are manufactured from PVC resins formed by the free radical polymerization of the vinyl chloride monomer (hydrochlorinated acetylene or ethylene reacted with chlorine). The homopolymer contains 57 pct Cl_2 by weight, slowly released at 200° C as hydrogen chloride and at rapid rates above 300° C. Dehydrochlorination of PVC is a complex elimination process, dependent on temperature and time, involving an "unzipping" operation with chlorine atoms as the chain carriers (*18*).

By contrast, the chlorinated fiberglass brattice, manufactured from an inorganic material (fiberglass higher than 90 pct) bounded with a silicon resin, is expected to release an extremely low amount of hydrogen chloride because of a low content of chlorinated additives.

Polyester-reinforced mine ventilation ducts are made of polyester resin, developed from the reaction of a dibasic acid (maleic or phthalic anhydride) with a dibasic hydric alcohol (propylene or ethylene glycol), blended with a reactive vinyl monomer (styrene, vinyl benzene, or vinyl toluene), reinforced (>80 pct) with fiberglass fibers, and treated with inhibitors (phenolic compounds) and flame retardants (chlorine, phosphorus, and antimony trioxide). The major drawback of the finished product is that it burns at fast rates (*19*), which causes the release of hydrogen chloride and carbon monoxide in large quantities.

EXPERIMENTAL SYSTEM

The system (fig. 1) consists of an approximately 20-L furnace whose temperature during experiments rises automatically from ambient (fig. 2) at a rate depending on the set furnace temperature, which varies from 100° to 1,200° C. The experimental temperatures are monitored continuously with type K thermocouples connected to a strip-chart recorder. A universal load cell, located under the furnace floor and contacted by the sample cup pedestal, transmits voltages of sample mass weight loss, via a bridge amplifier, to another strip-chart recorder. A vacuum pump draws ambient air continuously into the furnace (10 L/min), via an opening on the furnace door, and sends decomposition products in air, through a quartz tubing to the carbon monoxide, oxygen, and carbon dioxide analyzers and to the submicrometer particle detector analyzer (SPDA) (at 1.6 L/min) (*20*). During the embedded hydrogen chloride experiments, the decomposition air (10 L/min for a 14-min duration) was directed into the

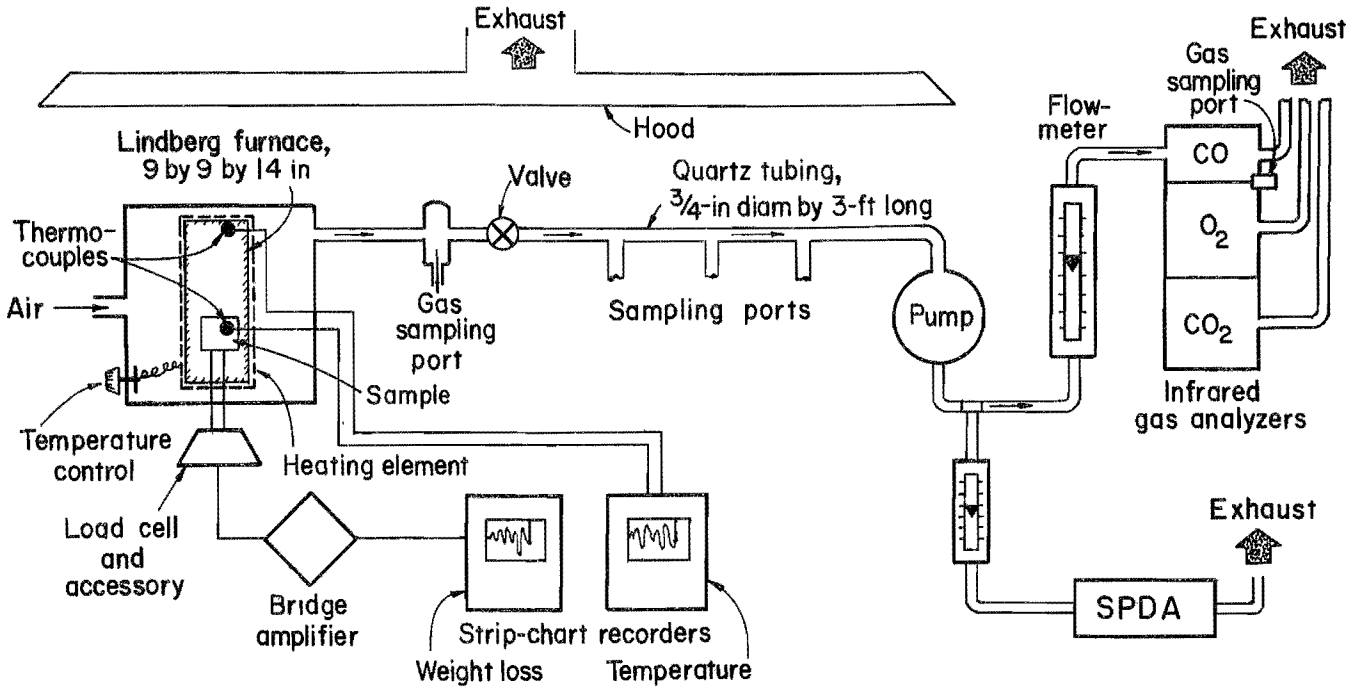

Figure 1.—Experimental system.

smoke particle filter placed between the quartz tubing and the pump. Flowmeters, installed between the pump outlet and the gas and particle analyzers, provide visual flow indication. Data (10 sec. interval) of sample and furnace temperatures, sample weight loss, and SPDA voltages are continuously acquired, mathematically treated, logged, filed, and displayed by means of a miniframe computer, via a laboratory-based real-time data acquisition system. Subsequently, the data are transferred into a data bank and plotted.

EXPERIMENTAL PROCEDURE

Two sets of experiments (six experiments in each set, each experiment repeated three times) were performed at set furnace temperatures of 250° and 1,000° C (fig. 2) for a 14-min duration, with 1-g samples of PVC (P1), neoprene (N1) and SBR (S1) mine conveyor belts; PVC (B1) and chlorinated fiberglass (F1) mine brattices; and chlorinated polyester-reinforced mine ventilation duct (D1). A third set of experiments (embedded hydrogen chloride experiments) was carried out at 1,000° C set furnace temperature only; under this set temperature (maximum furnace temperature reached at the 14th min, 600° C), the samples by decomposing completely release the largest amount of smoke particles on whose surface HCl embeds itself. A list of the materials is reported in table 1. A 1-g sample was placed in a 2.5-cm-diam sample cup, and the furnace was set at the desired temperature with a furnace airflow of 10 L/min; the decomposition air was directed into the gas analyzers, into the SPDA, and into the exhaust hood. As reported earlier, during the embedded hydrogen chloride experiments the airflow was directed into the smoke particle filter. The embedded hydrogen chloride on smoke particles, collected on filter, was determined by analysis of filter samples for hydrochloric acid and analyzed by ion chromatography. Hydrogen chloride gas concentrations were determined by short-term exposure tubes. The chlorine content of the material was determined by the American Society for Testing and Materials (ASTM) oxygen-bomb-combustion-selective-electrode method. Syringe grab samples, stored in sealed containers, were analyzed for carbon monoxide, carbon dioxide, and oxygen concentrations by gas chromatography. Other variables measured, as a function of time, were furnace temperatures, sample weight loss, and SPDA initial (without smoke) and experimental (with smoke) voltages.

Table 1.—Materials investigated

Material	Description	Cl_2, pct
Conveyor belt:		
PVC (P1)	Polymer component is PVC with fillers	23
Neoprene (N1)	Polymer component is neoprene rubber with fillers	11
SBR (S1)	Styrene-butadiene rubber with chlorinated additives	5
Brattice:		
PVC (B1)	Polymer component is PVC with fillers	28
Fiberglass (F1)	Fiberglass (>90 pct) fibers treated for fire retardancy with chlorinated additives.	5
Ventilation duct (D1)	Polyester resin reinforced(>80 pct) with fiberglass fibers, treated for flame retardancy with chlorinated additives and antimony trioxide.	10.5

PVC Polyvinyl chloride.
SBR Styrene-butadiene rubber.

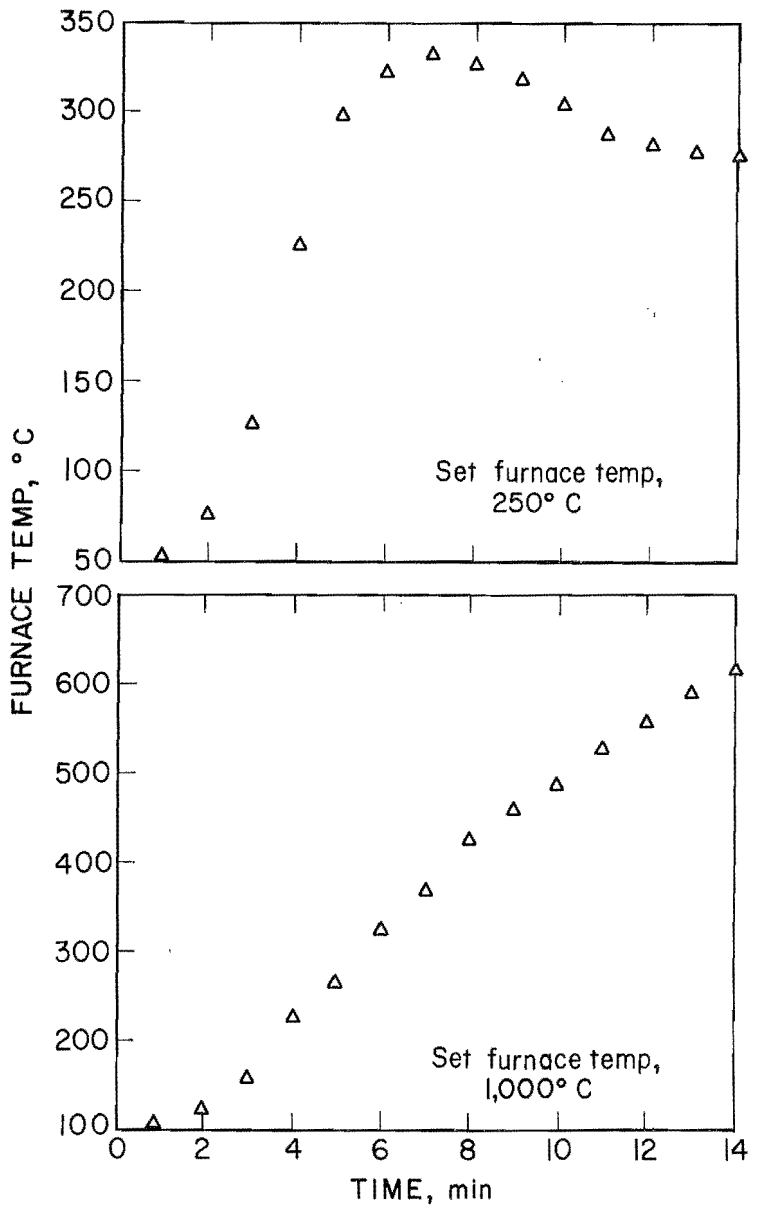

Figure 2.—Furnace temperature versus time at set furnace temperatures of 250° and 1,000° C.

DATA REDUCTION AND ANALYSES

At 250° C set furnace temperature and 14-min duration, representing the early stage of combustion at which most of the hydrogen chloride evolves with no gross degradation of the sample, hydrogen chloride gas concentrations (parts per million) were measured. The hydrogen chloride concentrations observed at 0.1 g of sample weight loss, adjusted to 1 g of weight loss, yielded the hydrogen chloride gas load (parts per million per gram). The load value, derived at a specific time and airflow, is an important toxicological parameter because it establishes, a priori, the maximum concentrations expected to evolve. Also, under the 250° C conditions, the smoke particle average diameter, d_g (centimeters, converted to micrometers), and particle concentration, n_o (particles per cubic centimeter), and the product of the smoke particle diameter and concentration, $d_g n_o$ (particles per square centimeter), were measured. The $d_g n_o$ was obtained from the ratio of the SPDA experimental and initial current output (Ie/Io) following the relationship in equation 1 (see also figure 3).

$$Ie/Io = 1/(K\, d_g n_o)\,(1 - \exp(-K\, d_g n_o)) \qquad (1)$$

where K = charging constant (0.012, cm^2/p).

Once the $d_g n_o$ is determined, d_g can be obtained from equation 2.

$$d_g = (\exp(aIc/d_g n_o) - 1)/Ic, \qquad (2)$$

where Ic = SPDA charged particle current,

and a = constant.

The $d_g n_o$ values observed during each experiment, adjusted to 1 g of sample mass weight loss, yielded the $d_g n_o$ load values (particle per square centimeter per gram), from which its inverse $1/d_g n_o$ load (square centimeters per particle per gram) was derived. Sample mass weight loss (grams), carbon monoxide (parts per million), carbon dioxide (parts per million), and oxygen (percent) concentrations, and furnace temperatures (degrees Celsius) were also measured. The carbon monoxide concentration observed at 0.1-g sample mass weight loss and adjusted to 1 g of weight loss yielded the carbon monoxide load (parts per million per gram).

At 1,000° C set furnace temperature and 14-min duration, the embedded hydrogen chloride (micrograms) and mass particulate (milligrams) captured on filters were

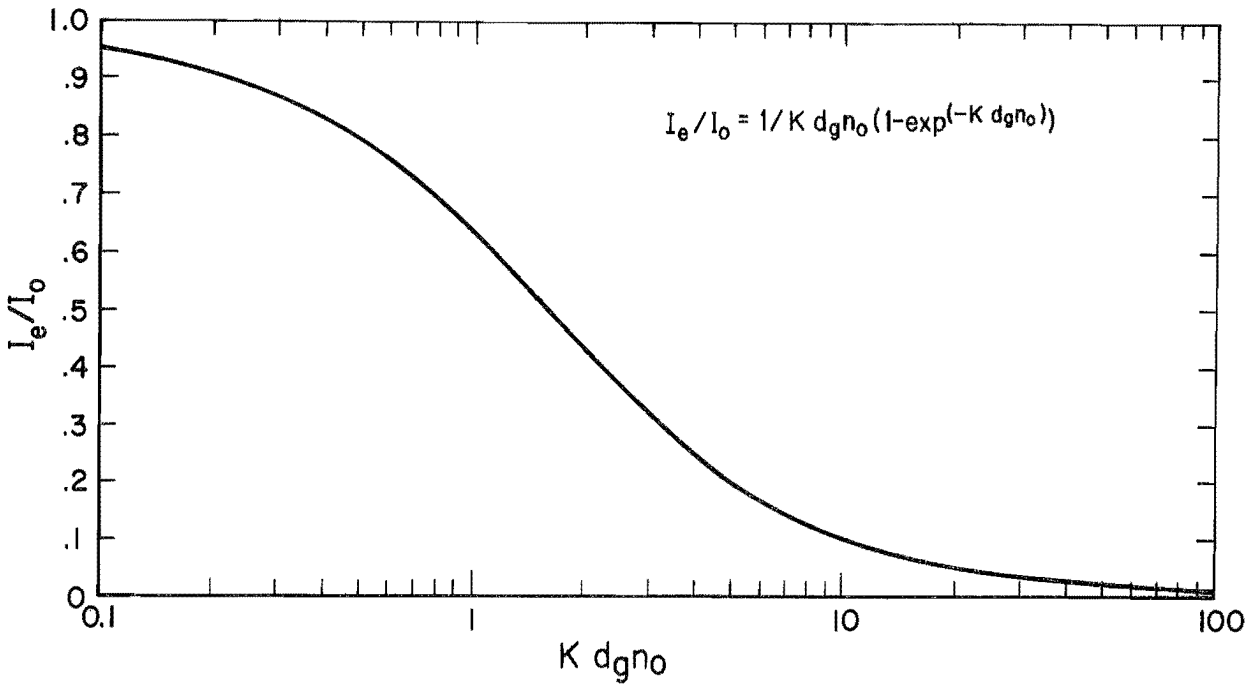

Figure 3.—SPDA current ratio (Ie/Io) as function of smoke particle diameter-concentration product ($d_g n_o$).

measured, and their loads (embedded hydrogen chloride, micrograms per gram; mass particulate, milligrams per gram) were derived. Actually, the embedded hydrogen chloride and mass particulates experimental values were treated as load values because of complete decomposition of the 1-g sample. Also, under the 1,000° C conditions, the smoke particle average diameter, d_g, and concentration, n_o, the sample mass weight loss, carbon monoxide, carbon dioxide and oxygen concentrations, and the furnace temperatures were measured.

RESULTS AND DISCUSSION

At 250° C set furnace temperature, PVC brattice B1 and PVC belt P1, followed by far by neoprene belt N1, released the highest hydrogen chloride gas concentrations because of the high chlorine content of the material, the lowest amount of smoke particles yielding the highest hydrogen chloride gas loads and the lowest $d_g n_o$ values, or the highest of its inverse, $1/d_g n_o$ (tables 2 and 3 and figure 4). Evidently, the higher and more rapid the hydrogen chloride release, the lower the number of solid particles available to the SPDA. By contrast, fiberglass brattice F1, followed by SBR belt S1 and ventilation duct D1, released the lowest hydrogen chloride gas concentrations because of the low content of chlorinated additives, and the largest amount of smoke particles yielding the lowest hydrogen chloride gas loads and the lowest $1/d_g n_o$ values. Under these conditions, small carbon monoxide concentrations were released by all samples, although the concentrations released by the PVC materials were somewhat larger because of larger weight loss (table 4). Large carbon monoxide loads, however, were derived for all samples. These loads were released in full at higher temperatures because of complete decomposition of the samples; exceptions, however, were observed for the fiberglass reinforced materials, whose large fiber content never decomposed.

Table 2.—Toxic load data at 250° and 1,000° C

(Furnace airflow, 10 L/min)

Material investigated[1]	250° C			1,000° C	
	HCl gas, ppm/g	CO, ppm/g	$1/d_g n_o$, $cm^2/(p \cdot g)$	Embedded HCl, μg/g	Mass particulate, mg/g
P1	1,350	1,580	0.004	289	2.4
N1	400	1,900	.0002	86	1.50
S1	200	1,250	.0003	29.7	1.2
B1	1,500	1,740	.005	292	3.0
F1	120	1,600	.0001	30	.92
D1	300	1,300	.0004	52	.87

[1]1-g sample. See table 1 for description.

Also, as shown in table 3 and in figures 5 and 6, PVC brattice B1 and PVC belt P1, followed, by far, by neoprene belt N1, released particles diameter with submicrometer. In figure 7, the irregular shape of PVC belt P1 smoke particles, as seen under the electron microscope, is shown at both set furnace temperatures. By contrast, fiberglass brattice F1, followed by SBR belt S1 and ventilation duct D1, released smoke particles with the largest diameter.

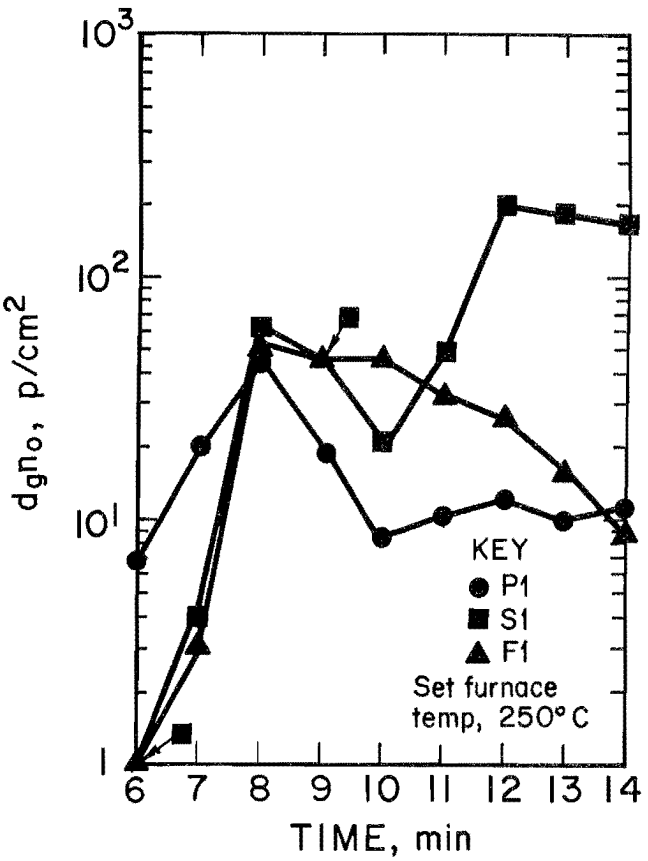

Figure 4.—Smoke particle diameter-concentration product ($d_g n_o$) versus time at set furnace temperature of 250° C. (See table 1 for description of materials investigated.)

Table 3.—Comparison of smoke particle characteristics data at 250° and 1,000° C

(Furnace airflow, 10 L/min)

Material investigated[1]	250° C					1,000° C				
	Time, min	d_g, μm	n_o, p/cm^3	$d_g n_o$, p/cm^2	Temp, °C	Time, min	d_g, μm	n_o, p/cm^3	$d_g n_o$, p/cm^2	Temp, °C
P1	6	0.7	123,000	7	250	6	0.023	425,000	1	290
	8	.5	903,000	48	300	8	.05	15,000,000	83	325
	9	.2	1,290,000	19	295	9	.03	126,000,000	239	400
	10	.04	3,300,000	9	290	10	.009	517,000,000	362	440
	12	.06	2,400,000	12	273	12	.004	582,000,000	288	500
	14	.04	2,860,000	11	260	14	.007	509,000,000	352	545
N1	6	0	0	0	250	6	0	0	0	289
	8	.12	389,000	19	308	8	.16	23,700,000	112	325
	9	.22	2,940,000	55	300	9	.008	267,000,000	244	402
	10	.11	7,900,000	83	294	10	.48	1,470,000	35	440
	12	.07	13,500,000	93	276	12	.17	1,470,000	25	500
	14	.1	97,800	101	262	14	.17	1,650,000	27	550
S1	6	.001	690,000	1	252	6	.3	660,000	10	290
	8	.5	1,270,000	63	303	8	.36	661,000	20	325
	9	.34	2,830,000	59	298	9	.06	139,000,000	228	400
	10	.37	628,000	22	295	10	.003	200,000,000	143	460
	12	.05	45,550,000	207	278	12	.008	364,000,000	310	480
	14	.06	30,300,000	189	265	14	.02	189,000,000	277	549
B1	6	.76	359,000	27	251	6	.28	2,740,000	35	289
	8	.2	5,270,000	88	302	8	.06	75,000,000	172	328
	9	.33	1,560,000	43	299	9	.21	3,280,000	5	406
	10	.21	3,430,000	61	294	10	.07	2,350,000	12	443
	12	.2	2,790,000	54	276	12	.29	52,800,000	29	509
	14	.25	963,000	43	264	14	.05	30,600,000	71	548
F1	6	5.1	2,100	1	250	6	4.7	34,500	16	250
	8	9.0	78,500	50	305	8	.35	6,500,000	145	348
	9	4.6	131,000	56	302	9	.04	75,600,000	280	392
	10	5.5	103,000	49	296	10	.03	102,000,000	302	432
	12	18	20,000	29	281	12	10	21,700	22	507
	14	50	554	10	268	14	4	71,600	27	573
D1	6	.003	363,000	1	244	6	.07	6,300	1	207
	8	.09	666,000	2	304	8	1.5	205,000	28	304
	9	.12	333,000	3	302	9	.4	4,230,000	90	347
	10	.05	646,000	3	295	10	.02	165,000,000	251	386
	12	.006	5,440,000	3	282	12	.25	6,450,000	51	423
	14	.003	8,510,000	3	268	14	.08	6,010,000	22	553

[1]1-g sample. See table 1 for description.

NOTE.—These concentrations evolved during the combustion of extremely small quantities of the samples.

Table 4.—Comparison of oxidative thermal degradation data at 250° and 1,000° C

(Furnace airflow, 10 L/min)

Material investigated[1]	250° C						1,000° C					
	Time, min	CO, ppm	O_2, pct	CO_2, ppm	Total WL, g	Temp, °C	Time, min	CO, ppm	O_2, pct	CO_2, ppm	Total WL, g	Temp, °C
P1	6	16	20.7	650		264	6	6	20.86	630		264
	8	156	20.8	800		322	8	617	20.7	1,300		363
	9	224	20.8	730	0.38	320	8	900	20.51	2,000	0.85	400
	10	128	20.8	810		314	10	1,370	20.5	2,300		447
	10	66	20.8	710		298	12	1,480	20.6	2,700		522
	14	20	21	610		283	14	340	20.6	2,300		588
N1	6	118	20.7	1,200		264	6	7	20.8	540		264
	8	120	20.8	1,500		319	8	106	20.7	980		363
	9	140	20.7	1,600	.18	315	9	400	20.6	1,600	.65	440
	10	150	20.7	1,800		309	10	486	20.5	1,840		447
	12	199	20.8	2,000		294	12	1,030	20.5	2,470		522
	14	150	20.8	2,300		283	14	403	20.5	2,600		588
S1	6	20	20.6	1,000		264	6	1	20.8	620		264
	8	134	20.7	1,200		319	8	264	20.7	800		303
	9	120	20.7	1,300	.14	315	9	1,000	20.5	1,400	.75	400
	10	100	20.7	1,400		309	10	1,470	20.5	1,320		447
	12	50	20.8	1,500		294	12	1,000	20.5	2,820		522
	14	20	20.7	1,200		283	14	453	20.6	2,570		588
B1	6	12	20.9	550		264	6	13	20.7	1,700		268
	8	66	20.9	800		322	8	282	20.7	2,400		366
	9	224	20.8	730	.56	320	9	630	20.6	2,600	.96	400
	10	88	20.8	810		314	10	743	20.5	2,800		490
	12	36	20.8	710		298	12	1,420	20.5	3,000		524
	14	20	21	610		283	14	313	20.5	3,600		588
F1	6	8	20.9	600		269	6	10	20.8	660		264
	8	14	20.9	560		320	8	33	20.8	700		363
	9	16	20.8	580	.01	325	9	42	20.8	710	.02	407
	10	13	20.8	576		314	10	72	20.8	740		447
	12	11	20.9	570		295	12	167	20.7	740		522
	14	8	20.9	560		290	14	125	20.7	740		588
D1	6	6	21	500		266	6	106	20.8	700		280
	8	9	20.8	500		320	8	508	20.7	710		380
	9	25	20.8	550	.13	318	9	600	20.7	990	.41	430
	10	60	20.8	550		311	10	1,100	20.7	1,200		450
	12	18	21	520		295	12	520	20.7	1,100		530
	14	12	20.8	500		280	14	320	20.7	1,100		600

WL Weight loss.

[1] 1-g sample. See table 1 for description.

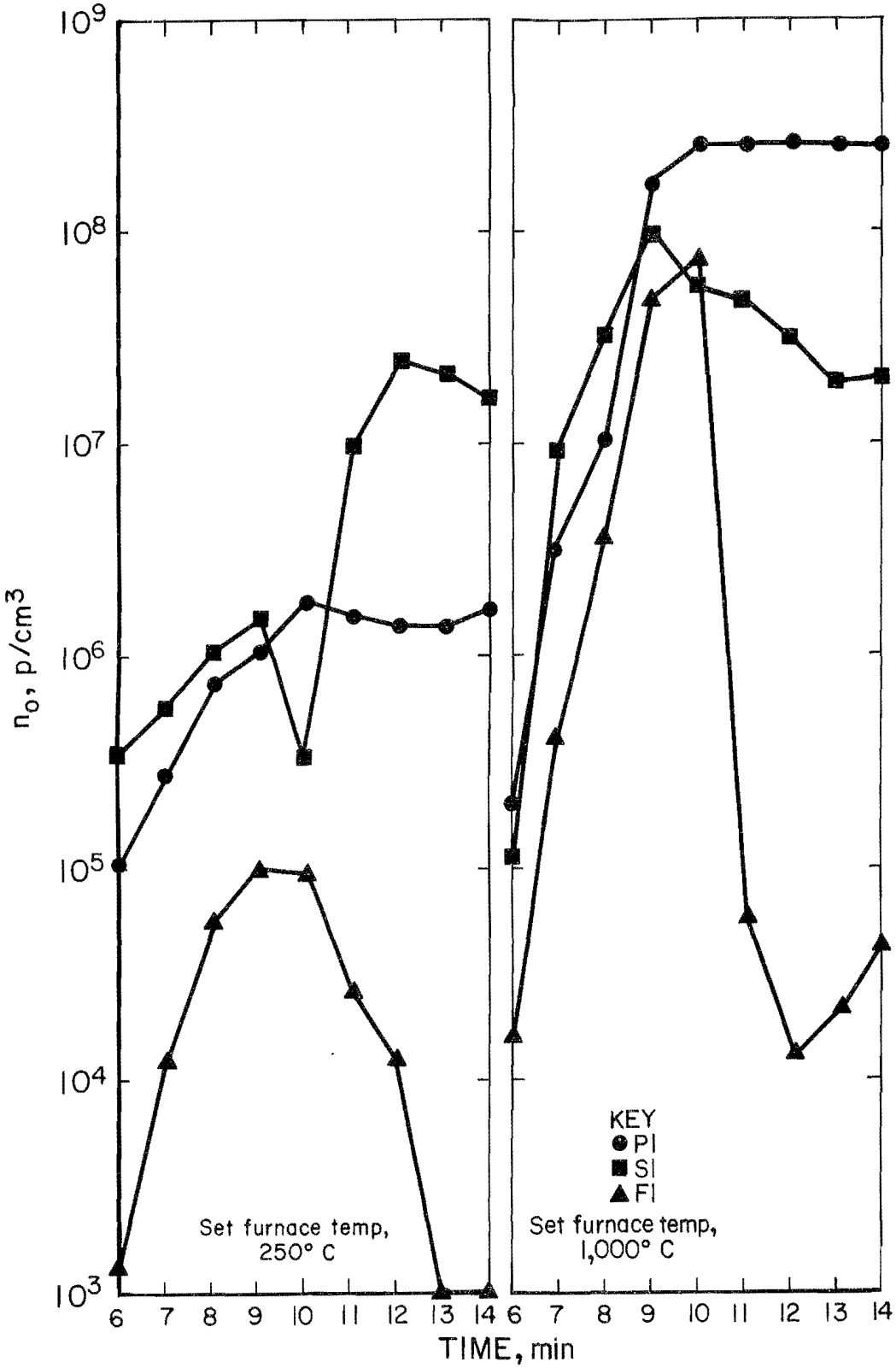

Figure 5.—Smoke particle concentration (n_o) at set furnace temperatures of 250° and 1,000° C. (See table 1 for description of materials investigated.)

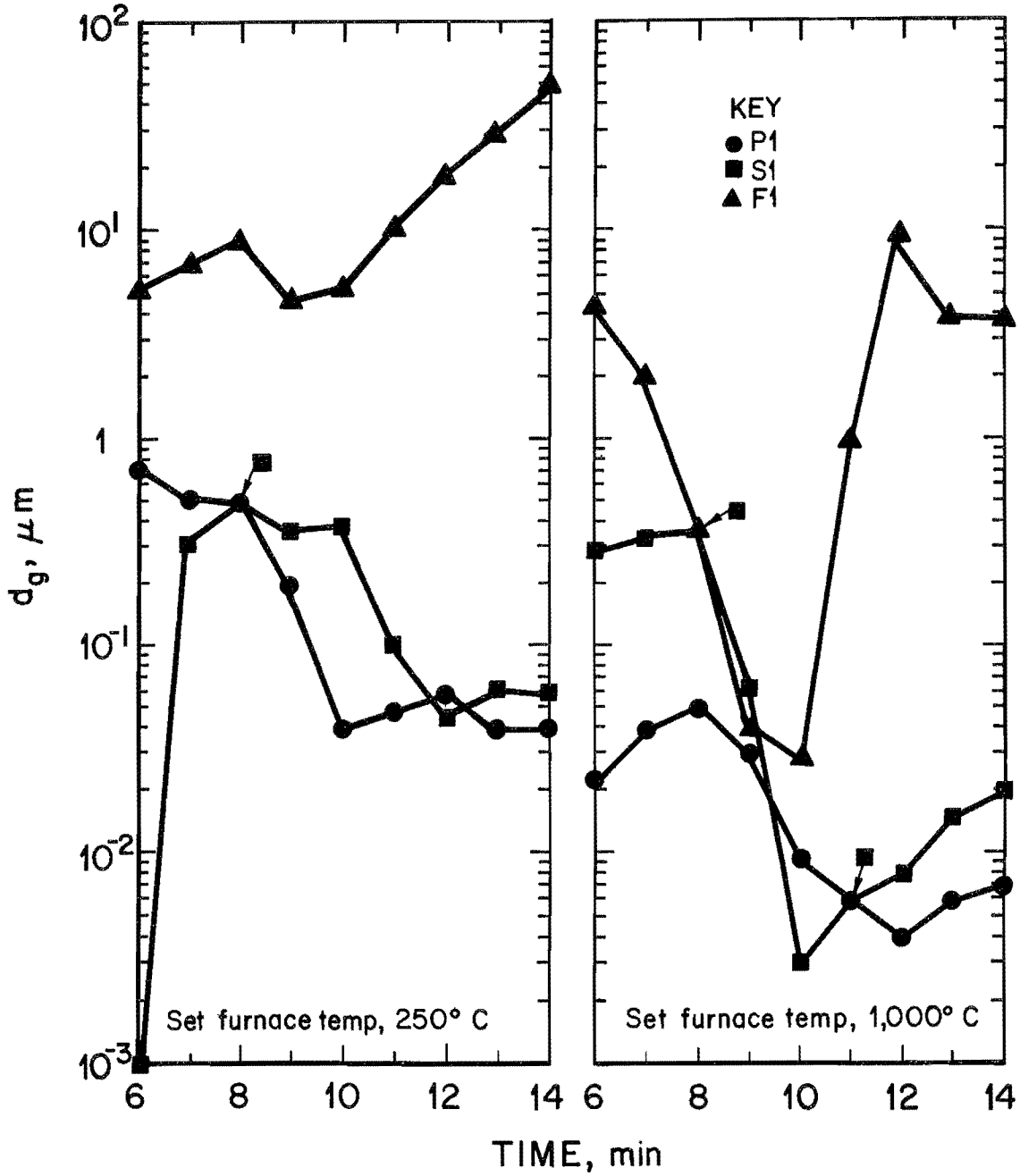

Figure 6.—Smoke particle average diameter (d_g) at set furnace temperatures of 250° and 1,000° C. (See table 1 for description of materials investigated.)

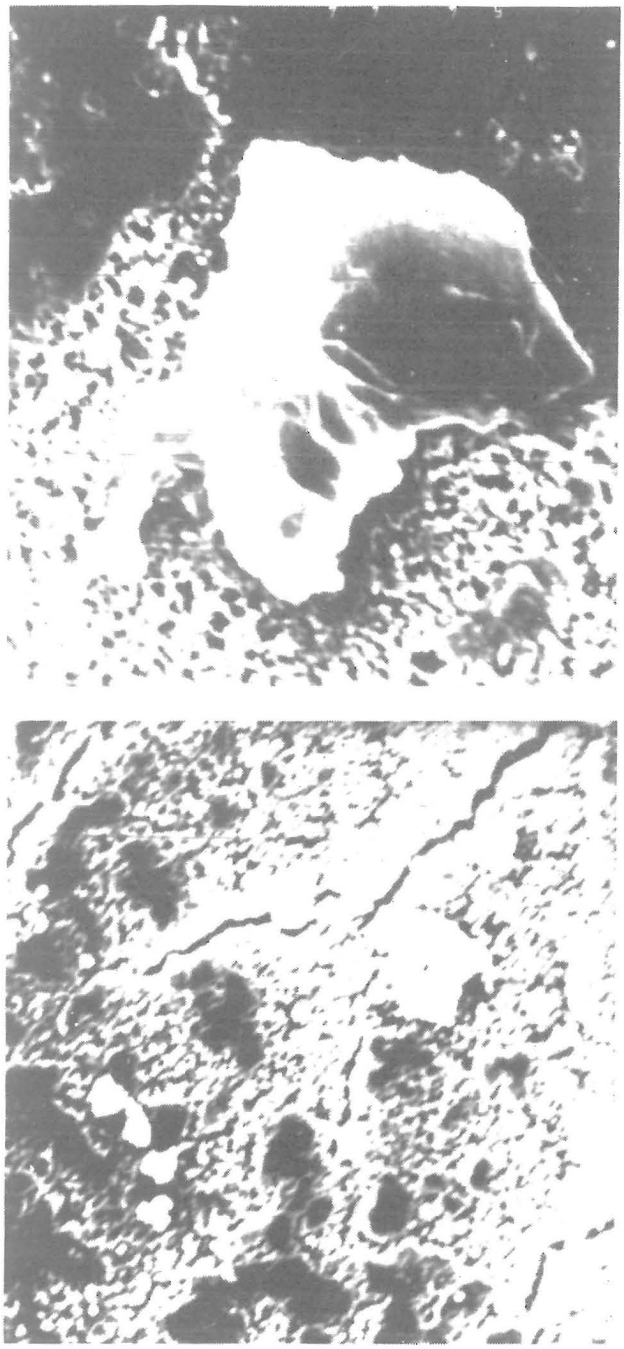

Figure 7.—Smoke particles (× 1,000) during combustion of PVC belt at set furnace temperatures of 250° (top) and 1,000° C (bottom) as seen under scanning electron microscope.

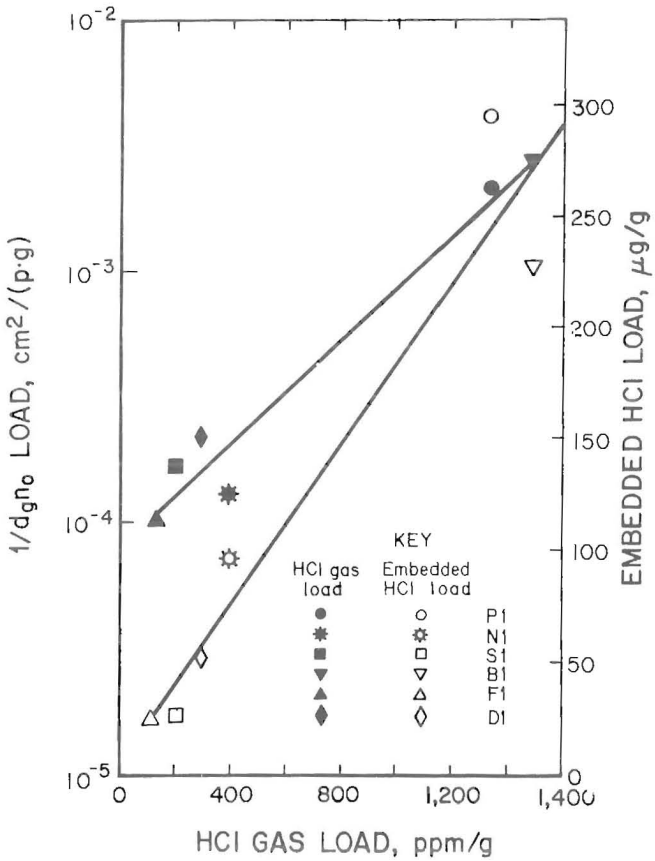

Figure 8.—Inverse of smoke particle diameter-concentration product ($1/d_g n_o$) load versus hydrogen chloride gas load and versus embedded hydrogen chloride load. (See table 1 for description of materials investigated.)

At 1,000° C set furnace temperature, PVC brattice B1 and PVC belt P1, followed by neoprene belt N1, yielded the highest concentrations of embedded hydrogen chloride, mass particulates, and submicrometer smoke particles (tables 2 and 3 and figures 5 and 6). The PVC materials also yielded the highest carbon monoxide concentrations because of large weight loss (table 4). Evidently, under these conditions, for this type of materials, a large amount of hydrogen chloride in the gaseous and aerosol phase and a large amount of particles on whose surface hydrogen chloride droplets embed themselves are available. By contrast, the lowest concentrations of embedded hydrogen chloride, mass particulates, and smoke particles were released by fiberglass F1, SBR S1, and ventilation duct D1. These types of materials also yielded the lowest carbon monoxide concentrations because of lower weight loss, which in the case of the fiberglass brattice and ventilation duct is due to the high content of inorganic fibers. A direct dependence exists between the embedded hydrogen chloride loads observed under the 1,000° C conditions and the hydrogen chloride gas loads derived under the 250° C conditions. Both types of loads are directly correlatable to the $1/d_g n_o$ loads; the higher the hydrogen chloride gas load, the higher the embedded hydrogen chloride load, the higher the $1/d_g n_o$ load value.

Correlations were established ($r > 0.88$) between the $1/d_g n_o$ values, the hydrogen chloride gas loads, and the embedded hydrogen chloride loads (fig. 8). As shown in table 2, PVC brattice B1, with a hydrogen chloride gas load of 1,500 ppm/g, and PVC belt P1, with a hydrogen chloride gas load of 1,350 ppm/g, yielded the highest embedded hydrogen chloride loads of 292 and 289 μg/g, the highest $1/d_g n_o$ values of 0.005 and 0.004 cm^2/(p·g), and the largest mass particulate loads of 3 and 2.4 mg/g, respectively.

By contrast, the fiberglass brattice F1 and SBR belt S1, with hydrogen chloride gas loads of 120 and 200 ppm/g, yielded the lowest embedded hydrogen chloride loads of 30 and 29.7 μg/g, the lowest mass particulate loads of approximately 1 mg/g, and the lowest $1/d_g n_o$ values of 0.0001 and 0.0003 cm^2/(p·g), respectively.

CONCLUSIONS

According to our findings, the smoke particle characteristic $1/d_g n_o$ is predictive of the embedded hydrogen chloride on smoke particles evolved during combustion of PVC and chlorinated mine materials. The embedded hydrogen chloride is directly dependent on the release of hydrogen chloride gas concentrations; the higher the hydrogen chloride gas concentrations, the higher the embedded hydrogen chloride on smoke particles, the higher the $1/d_g n_o$ values.

The PVC mine conveyor belt (P1) and the PVC mine brattice (B1), followed by far by the neoprene belt (N1), yielded the highest hydrogen chloride gas concentrations because of the high chlorine content of the materials, the highest embedded hydrogen chloride, and the highest $1/d_g n_o$ values. During the combustion of these types of materials, hydrogen chloride is released early, and as the temperature rises, large quantities of particulates, on which hydrogen chloride droplets embed themselves, are released. By contrast, the fiberglass brattice (F1), followed by the SBR belt (S1) and the ventilation duct (D1), yielded the lowest hydrogen chloride gas concentrations because of the low content of chlorinated additives, the lowest embedded hydrogen chloride, and the lowest $1/d_g n_o$ values.

The excellent correlation between the smoke particle characteristic $1/d_g n_o$, the hydrogen chloride gas concentrations, and the embedded hydrogen chloride suggests its development and use as a testing parameter to assess the toxic hazard of PVC and chlorinated materials during fire.

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